PARYLENE ETCHING TECHNIQUES FOR MICROFLUIDICS AND BIOMEMS

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ABSTRACT

Parylene C (poly(monochloro-*p*-xylylene)) is a member of a unique family of thermoplastic, crystalline polymers. Compared to other polymers, parylene films are exceptionally conformal and chemically inert owing to its vapor deposition polymerization (VDP) coating process. These properties bring about many interesting possibilities for MEMS, particularly in microfluidic and bioMEMS applications. Dry etching techniques are required to define fine features in parylene films. For the first time, selective parylene C removal using oxygen-based plasmas is characterized for plasma etching, reactive ion etching (RIE), and deep reactive ion etching (DRIE) based methods. The ability of these techniques to achieve high aspect ratio (HAR) structures desirable for MEMS applications is also investigated.

1. INTRODUCTION

Parylene as a MEMS Material

Parylene is the generic name for a family of unique vapor phase deposited polymers. It was originally discovered by Michael Mojzesz Swarc in 1947 and commercialized by Union Carbide Corporation in 1965 after the development of a practical deposition process by William F. Gorham [1]. Although over 20 types of parylene have been developed, only three are commonly available (Fig. 1).

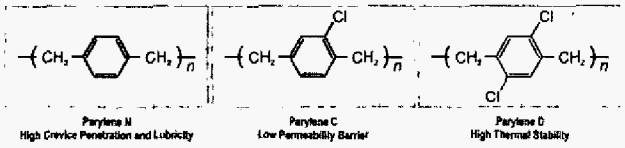

Figure 1: Commercially available types of parylene

Parylene has found wide acceptance in the microelectronics and medical industries as a coating material. Recently, much attention has been given to parylene by MEMS researchers in applications ranging from microstructures to integrated microfluidic systems [2-6]. The need for biocompatible materials has driven the popularity of polymers for MEMS. Among them, parylene has particularly attractive properties including low process temperature, low defect density, transparency, and chemical inertness. In addition, parylene technology can accommodate multi-layer processing to produce complex structures and features (Fig. 2).

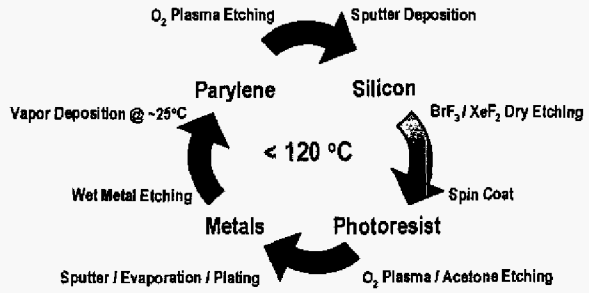

Figure 2: Low-temperature, multi-layer parylene processing technology for MEMS

Biocompatibility of Parylene

Parylene has attracted a great deal of interest due to its biocompatibility and biostability. Biological environments are extremely corrosive to most MEMS and microelectronic materials however it does not affect parylene as it cannot be degraded hydrolytically [7]. In addition, parylene has low cytotoxicity which has lead to its application as a platform for neural growth [8, 9].

2. SELECTIVE PARYLENE REMOVAL

Chemical Removal

Parylene resists dissolution by solvents at temperatures below its melting point. Although it is possible to dissolve parylene in chloronaphthelene or benzolyl benzoate at temperatures above 150 °C [10], this technique is incompatible with commonly used lithographic processes. Lift-off is also problematic due to the highly conformal nature of parylene films. Sabeti [11] reported the possibility of selectively depositing parylene by creating heat using localized resistors. UV laser ablation of parylene has also been demonstrated [12, 13]. However, the only practical method to pattern parylene is through plasma etching.

Plasma Removal

Previously, plasma [14, 15], reactive ion beam (RIBE) [16], and reactive ion [17, 18] etching of parylene in oxygen environments has been reported. Parylene film thicknesses of only a few microns were etched and no attempt at HAR structures was made. Yeh [17] has observed that etch selectivity between parylene and standard photoresist masking materials is near unity due to their organic nature.

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Majid [18] reported that etching parylene by RIE using low pressure and power with a substrate bias gave rise to trenches with vertical profiles, however these same conditions resulted in surface roughness of the etched features. Specifically, delicate and dense micrograss structures were observed on the parylene surface. Ratier [16] noticed that RIBE gave better surface uniformity than RIE however the etch rates are very low (~15-55 Å/m).

Zahn [19] reported achievable aspect ratios of 20:1 by employing Bosch-like switching chemistries for the etching of polymethylmethacrylate (PMMA). Standaert [20] demonstrated vertical sidewalls in parylene N using an inductively coupled plasma source. Based on these promising results, a similar technique has been demonstrated to etch parylene and photoresist.

Plasma Etching Mechanisms

The mechanisms that govern parylene etching processes are not well understood. A possible mechanism for etching parylene N using a microwave plasma source was reported [21]. The proposed etching mechanism involves the opening of the benzene ring brought about by the following sequence of reactions: (1) hydrogen abstraction from the ethyl carbons between the benzene rings in the polymer chain, (2) molecular or atomic oxygen adsorption onto the exposed reactive site, (3) polymer degradation through the formation of volatile carbon monoxide (for atomic oxygen adsorption) or dioxide (for molecular oxygen adsorption), and (4) radical site formation on the aromatic ring. The parylene C etching mechanism is believed to be similar to that for parylene N. Chemically, their structures differ by the presence of a chlorine atom in parylene C which reduces the exposed carbon bonding sites by one. This may correspond to the observed reduction in etch rate by approximately 17 % [22].

3. EXPERIMENTAL METHODS

Silicon test coupons measuring 20 mm × 10 mm were manually separated from a wafer coated with 10 μm of parylene and masked by 14 μm of AZ 4620 photoresist. Coupons were etched using plasma (Technics PEII-A), RIE (The Semi Group RIE System 1000 TP/CC), and DRIE (PlasmaTherm SLR-770B) modes under varying conditions. Etch rates of parylene and the photoresist masking layer were obtained for varying pressure, gas flow, power, and etching chemistries. In addition, programmed switching chemistries were examined for DRIE mode. Each etching cycle, or loop, consists of two steps: (1) deposition of C_4F_8 and (2) O_2 etching, where the fluoropolymer layer protects feature sidewalls from lateral etching. Sputtered amorphous silicon (0.5μm) and oxide (0.3μm) were also examined as possible masking materials. After etching, step heights were measured using a surface profile (Tencor AlphaStep 200). The photoresist was stripped from half of the etched sample and profiled again to determine the etch rates for parylene and photoresist.

4. RESULTS AND DISCUSSION

Plasma etching results exhibit increasing etch rate for increasing power (Fig. 3). However, the etch rate decreases for increasing pressure. Generally, the etch rate increases with flow rate (flow limited regime), reaches a maximum, then decreases for higher flow rates. This decrease is attributed to the pumping speed whereby the active species is removed before it can react [23].

Similar trends are observed for RIE and DRIE (Fig.s 4-5). The effects of adding argon to the oxygen plasma and using switched chemistries in DRIE mode were also examined (Fig.s 6-7). The addition of Ar is thought to contribute to the etch rate through physical sputtering. Here, however, it reduces the etch rate. The effect of flow limited etching is apparent for both etch step time settings at low flow. The highest etch rates are obtained for oxygen flows of 100 sccm in RIE mode which corresponds to the maximum flow rate limit of the etching

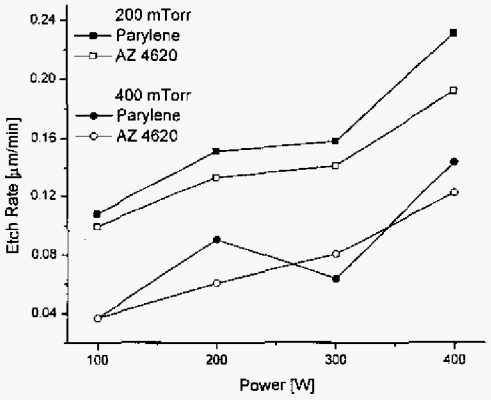

Figure 3: Etch rates of parylene and AZ 4620 for varying power and pressure by plasma etching

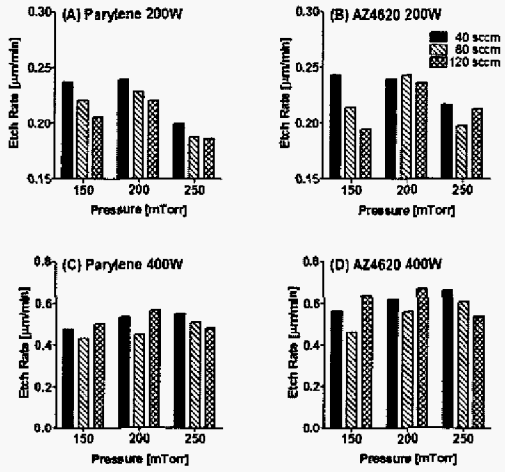

Figure 4: Etch rates of parylene and AZ 4620 for varying power and pressure in oxygen plasma by RIE

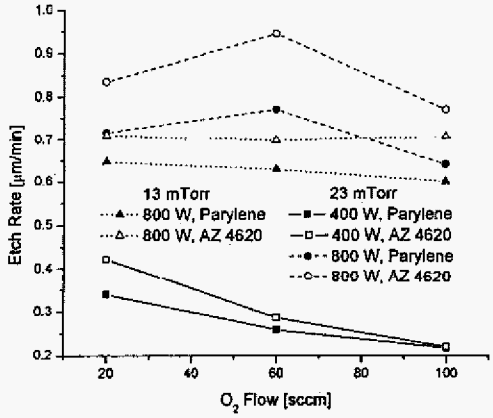

Figure 5: Etch rates of parylene and AZ 4620 for varying power and pressure in oxygen plasma by DRIE

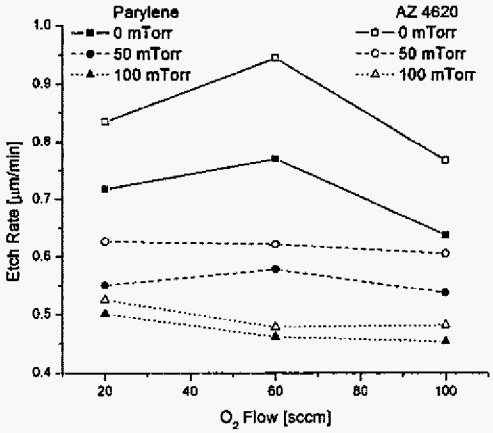

Figure 6: Etch rates of parylene and AZ 4620 for varying power and pressure in oxygen and argon plasma by DRIE

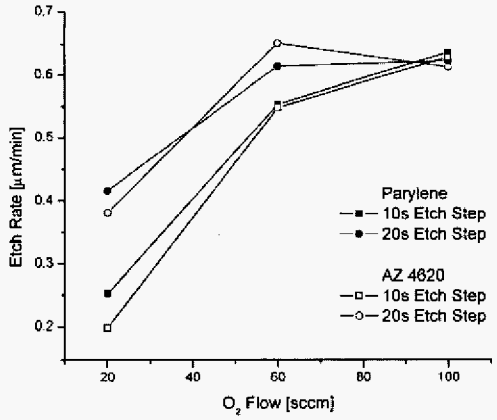

Figure 7: Etch rates of parylene and AZ 4620 for switched chemistry etching by DRIE

apparatus. It is possible that etch rates obtained using DRIE may be higher than that of RIE as the data does not subtract the etch time required to remove the deposited fluorocarbon sidewall protection layer. Recipes and results for maximum parylene and photoresist etch rates are summarized in Table 1. Etch selectivity remains a drawback of using photoresist masks for all methods examined. Sputtered α-silicon and oxide masks also perform poorly in DRIE switched chemistry etching due to poor adhesion and etching, respectively. Others have tried spin-on glass and nitride masks with some success [20].

Table 1: Maximum observed etch rates and respective etching conditions for parylene and AZ 4620 for various etch methods

	Parylene	AZ 4620
Plasma (200 mT, 400 W)	.19 μm/min	.29 μm/min
RIE (100 sccm, 200 mT, 400 W)	.56 μm/min	.67 μm/min
DRIE (60 sccm, 23 mT, 800 W)	.77 μm/min	.94 μm/min

Profiles of features etched using plasma, RIE, and DRIE techniques are compared in Fig. 8. Plasma etched samples exhibited significant lateral etching and tapered profiles whereas DRIE switched chemistry etching produces nearly vertical sidewalls. Preliminary results indicate that aspect ratios of at least 2:1 can be achieved for etching parylene with both RIE and DRIE. Traditional oxygen plasma etching techniques yield at best a ratio of 1:1. With DRIE it is also possible to produce tapered, vertical, or reentrant sidewall profiles, which suggests interesting possibilities for using etched parylene features for molding applications. Further improvement of etched aspect ratio is expected with the application of a substrate bias in RIE and DRIE modes [18, 20]. It has also been reported that parylene etching can be enhanced by the addition of CF_4 [18].

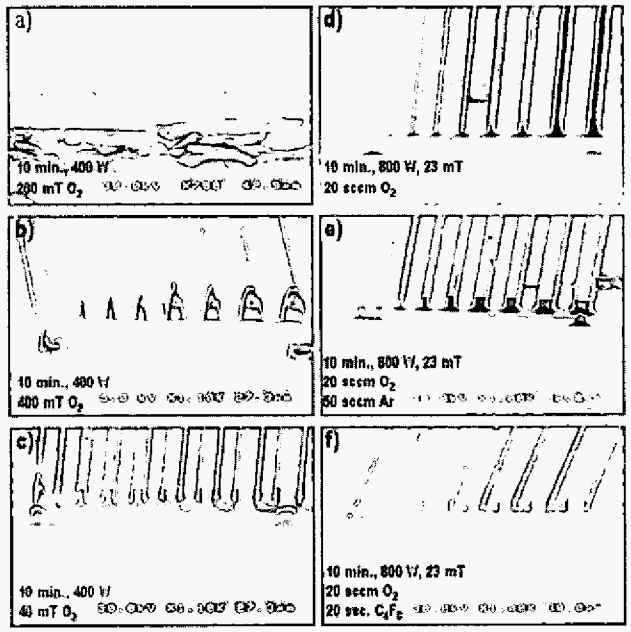

Figure 8: Etched parylene profiles of line features for plasma etching (a, b); RIE (c); DRIE oxygen only (d); DRIE oxygen and argon (e); and DRIE switched chemistry etching (f)

5. CONCLUSION

The etching of parylene C has been examined for plasma, RIE, and DRIE modes. Masking materials, etching chemistries, and process parameters (power, pressure, and gas flow) were varied to ascertain the effect on the etch rate and resultant feature profiles. Initial results are promising for the development of a process to produce HAR structures in parylene by using RIE and DRIE. Future studies involving the application of a substrate bias and different etching species are expected to further improve upon the results presented here.

6. ACKNOWLEDGMENTS

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